

CATALYTIC PARTIAL OXIDATION OF METHANE TO METHANOL AND FORMALDEHYDE

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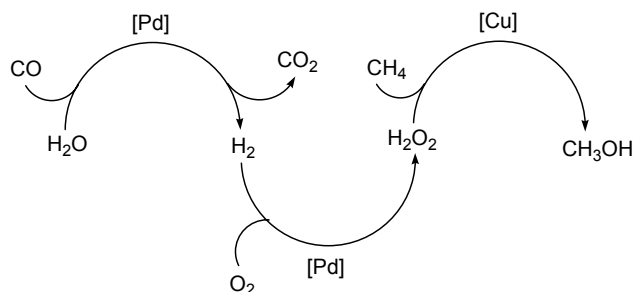
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Introduction

Methane is the least reactive and the most abundant member of the hydrocarbon family. Ethane comes second in both categories. Together, their known reserves approach that of petroleum [1]. Thus, the selective oxidative functionalization of these alkanes to more useful chemical products is of great practical interest [2-7]. The current technology for the conversion of alkanes to oxygenates involves *multi-step* processes. Clearly, the *direct* partial oxidation of the lower alkanes to oxygenates would be far more attractive from an economic standpoint. Of particular interest would be the formation of the *same* end product from different starting alkanes, thus obviating the need to separate the alkanes. For example, natural gas is principally methane with 5-10% ethane. A system that converts both to the same C₁ product, would not require the prior separation of the alkanes. We will discuss two catalytic systems for the direct partial oxidation of methane by dioxygen.

Results and Discussion

The first system involves the catalytic oxidation of methane to methanol by dioxygen in a mixture of water and trifluoroacetic acid [8,9]. A combination of metallic palladium and copper chloride acts as the catalyst and either carbon monoxide or dihydrogen is required as a coreductant. Studies indicate that the overall transformation encompasses three catalytic steps in tandem (Scheme 1). The first is the water gas shift reaction involving the oxidation of carbon monoxide to carbon dioxide with the simultaneous formation of dihydrogen. It is possible to bypass this step by replacing carbon monoxide with dihydrogen. The second catalytic step involves the combination of dihydrogen with dioxygen to yield hydrogen peroxide (or its equivalent). The final step involves the metal catalyzed oxidation of the alkane by hydrogen peroxide (or its equivalent). The activation parameters for the overall reaction, determined under the condition when the rate is first-order in both methane and carbon monoxide, are: $A = 2 \times 10^4 \text{ s}^{-1}$; $E_a = 15.3 \text{ kcal mol}^{-1}$.



Scheme 1. Proposed catalytic three-step mechanism for methane oxidation.

The role of metallic palladium is two-fold. First, it generates hydrogen peroxide (or its equivalent). Second, it causes non-

specific overoxidation of the substrate using the hydrogen peroxide thus generated. This latter reaction is suppressed when copper chloride is added; instead, copper chloride appears to catalyze the selective hydroxylation of the alkane by hydrogen peroxide. An interesting reactivity pattern exhibited by the bimetallic system is the preference for C-C cleavage over C-H cleavage for higher alkanes. Indeed, we are unaware of any other catalytic system that effects the oxidative cleavage of alkane C-C bonds under such mild conditions.

A curious aspect of the bimetallic system is that, apart from its ability to simultaneously activate both dioxygen and alkane, it requires a coreductant: carbon monoxide or dihydrogen. Thus, there is a striking resemblance with monooxygenases. In nature, while the dioxygenases utilize the dioxygen molecule more efficiently, it is the monooxygenases that carry out "difficult" oxidations, such as hydroxylation of alkanes. In the latter, one of the two oxygen atoms of dioxygen is reduced to water in a highly thermodynamically favorable reaction and the free-energy gained thereby is employed to generate a high-energy oxygen species, such as a metal-oxo complex, from the second oxygen atom.

The second catalytic procedure involves the gas-phase partial oxidation of methane and ethane to formaldehyde by dioxygen [10]. NO_x acts as catalyst and is *not* consumed in the reaction. The yield of oxygenates from methane is over 11%. The yield increases to over 16% when a trace of ethane (0.7%) is added to the gas mixture (Table 1). As might be expected, the yield of oxygenates from ethane is higher: over 24%. A catalytic cycle involving NO₂ as the C-H activating species is proposed (Scheme 2). The results that we have obtained thus far are noteworthy in several respects. First, the same C₁ product (formaldehyde) is obtained from both methane and ethane. Thus, the prior separation of the latter alkane is not required for this process. Second, in the context of partial oxidation of methane to oxygenates by dioxygen, there are few other system in the open literature that simultaneously exhibits such high conversion and selectivity.

Table 1. Methane Oxidation in Presence of Trace Ethane

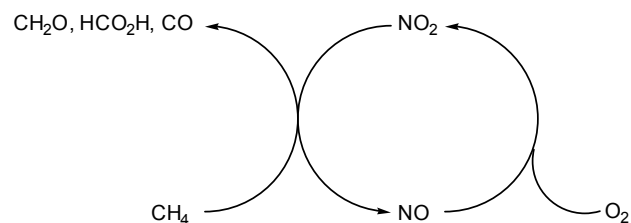
Experiment No.	1	2
Temperature, °C.	600	600
Flow rate, mL/sec	2.26	5.65
Yield of CH ₃ OH ¹ , %	---	1.00
Yield of CH ₂ O ¹ , %	13.96	15.30
Yield of HCO ₂ H ¹ , %	2.27	0.64
Yield of CO ¹ , %	14.26	8.50
Total conversion ¹ , %	30.5	25.4
Selectivity ² , %	53.2	66.5
Yield ³ , %	16.2	16.9
Total products, mmol.	3.08	6.21
[CH ₄ (inlet) – CH ₄ (outlet)] + CH ₃ CH ₃ x 2, mmol	3.23	5.82

Gas mixture: CH₄, (16.6%); CH₃CH₃, (0.7%); NO, (11.0%); O₂, (5.5%); N₂, (16.6%); He, (49.7%).

1. Based on total carbon in CH₄ and CH₃CH₃.

2. Selectivity: $\Sigma(\text{CH}_2\text{O} + \text{CH}_3\text{OH} + \text{HCO}_2\text{H})/\Sigma(\text{total products})$.

3. Yield: Total conversion x Selectivity.



Scheme 2. Proposed mechanism for NO_x -catalyzed methane oxidation.

References

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